Synthesis, characterization and application of nanoscale zero-valent iron in the degradation of the azo dye Disperse Red 1

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ABSTRACT

In this work, a multivariate response surface methodology (RSM), was applied to analyze the effects of the synthesis variables that affect the reactivity of nanosized zero valent iron particles (NZVI), obtained by chemical reduction with sodium borohidride on the decoloration of azo dye Disperse Red 1 (DR1). Statistical analysis and data interpretation revealed that the generated model showed significant regression and fitting. The conditions that generated NZVI with higher reactivity correspond to [Fe^{2+}]: [BH$_4^-$] molar ratio = 1:3, higher rates of reducing agent addition and lower pH (2–3). NZVI particles synthesized under the optimal conditions were characterized via XRD, BET surface area and electron microscopy. The results showed that the nanostructured material had composition, morphology and crystallinity typical of zero-valent iron, with BET surface area of 45 m^2 g^{-1} and an average particle size of 60 nm. NZVI yielded high color removal in fairly short time (around 98% in 10 min). Latter combination with H$_2$O$_2$ allowed high mineralization.

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1. Introduction

Red disperse 1 is an important synthetic dye widely used in industrial polyester dyeing processes. It has an azo group (—N=N—) which is the most unstable part and is responsible for its carcinogenicity, toxicity and biorecalcitrance [1,2]. For this reason, textile effluents contaminated with these dyes often hinder conventional treatment (aerated lagoons and activated sludge). The inefficiency of these processes is also demonstrated by the detection of dyes and their processing products in surface waters [3]. Thus, studies of the development of alternative and efficient methodologies for the degradation of this type of contaminant are required.

Nanosized zero valent iron (NZVI) particles can provide innovative solutions for the degradation of a wide range of pollutants in water, such as phenol [4], chlorophenols [5,6], *p*-chloronitrobenzene [7], dyes [8,9], and heavy metals [10–12], due to their specific surface area and high reactivity. Under anoxic conditions, NZVI emerge as a low-cost and effective solution for the reduction of nitro (NO$_2$—) and azo (—N=N—) groups, whereas under aerobic conditions they can generate hydroxyl radical, a non-selective oxidant able to mineralize pollutants like *p*-nitrophenol and dyes [13,14]. Obtaining highly reactive particles is the key issue for potential application and has been the research purpose of several studies. In this context, the literature reports several methodologies such as reduction of iron oxide with hydrogen at high temperature [15], thermal decomposition of iron pentacarbonyl [16] and reduction of dissolved iron salts in aqueous phase using sodium borohydride [17]. This last has become one of the most studied methods. Song et al. analized the effects of the synthesis conditions (reductant delivery rate, pH, [Fe^{3+}] and [BH$_4^-$] concentration) on the reactivity of nano-structured iron for chlorophenol dechlorination [18]. Yu-Hoon et al. [19] studied the dependence of morphology, surface area and reactivity respect to the synthesis variables of NZVI used for nitrate reduction. There is a general agreement in the literature in the sense that: (i) the reactivity of NZVI strongly depends on the pH of the synthesis solution, (ii) the higher the precursor concentration the higher the NZVI reactivity and (iii) the reactivity increases with the feeding rate of the reductant solution.

However, thus far research addressed to quantify the contribution of those variables to NZVI reactivity towards the degradation of chemical species of environmental relevance, has been quite limited and is generally associated with univariate studies, which therefore do not consider second or third-order interactions among experimental variables [7,9,17–19], which are useful for the establishment of empirical models with predictability potential.

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Additionally, although the qualitative relationship between typical independent variables of nanosized zero valent iron synthesis (iron salt reduction method with $NaBH_4$) is relatively clear, contributions that associate such conditions with reactivity and BET area may still be useful. In this context, the current work presents the results obtained by applying multivariate statistical methodology based on factorial design of experiments and response surface (RSM) to evaluate the effects of pH, iron precursor concentration and the rate of addition of the reducing agent on the reactivity of the resulting NZVI particles towards the degradation of the azo dye Disperse Red 1 (DR1) in water.

2. Materials and methods

2.1. Chemicals

All chemicals were purchased from Sigma–Aldrich (St. Louis, MO) and used as received without further purification, unless otherwise specified. These include ferrous sulfate (ACS reagent), sodium borohydride (98%), acetone (HPLC grade), ethanol (ACS reagent), hydrogen peroxide (ACS reagent), and DR1 azo dye (Empirical Formula: $C_{16}H_{18}N_4O_3$; Molecular Weight: 314.34; Dye content: 98% and λ_{max}: 502 nm). The DR1 solution (0.025 mM) was prepared at 90 °C under stirring for 30 min. All solutions were prepared with Deionized and deoxygenated water (18 $M\Omega$ cm) produced from Milli-Q (Millipore, USA). Deoxygenation was carried out by purging with N_2 for 3 h. The pH of the ferrous chloride solution and DR1 testing solution was adjusted with reagent-grade dilute hydrochloric acid and sodium hydroxide.

2.2. Synthesis of NZVIs

A ferrous chloride solution was prepared by dissolving $FeCl_2 \cdot 4H_2O$ salt in distilled water (purged with N_2). A solution of reducing agent (0.3 M) was prepared by dissolving sodium borohydride ($NaBH_4$) in distilled water. The reducing agent solution was then added to the Fe solution (via peristaltic pump) at a controlled rate, under continuous magnetic stirring and room temperature. Iron concentration, pH and the rate of addition of the reducing agent were adjusted according to experimental design shown in Table 1. Ferrous iron reduces to the zero-valent form according to:

$$Fe^{2+}_{(aq)} + 2BH_4^{-}_{(aq)} + 6H_2O_{(l)} \rightarrow Fe^0_{(s)} + 2B(OH)_{3(aq)} + 7H_{2(g)} \quad (1)$$
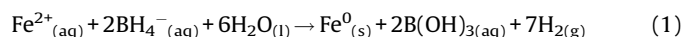
Black particles of zero-valent iron appeared immediately after adding the first few drops of the reducing agent solution. The resulting particles were washed, at least three times, with distilled water and absolute ethanol, separated by filtration and dried under inert atmosphere (glove-bag). Freshly prepared metallic particles were then characterized and immediately used in reaction without further treatment.

2.3. Experimental design

As indicated before, the aim of this work is to learn on how NZVI reactivity is affected by three independent variables: initial

concentration of Fe^{2+} (X_1), feeding rate of $NaHB_4$ solution (X_2) and pH (X_3). DR1 decoloration was the response. A 2k factorial design with six axial center points and two replicates at the center point has been used. The α value is ±1,68, calculated by:

$$\propto = \sqrt[4]{2^k} \quad (2)$$

where k is the number of independent variables.

According to this design, the total number of variables combinations is 2k + 2k + n, where n is the number of repetitions at the central point. That gives 16.

The equation relating the response (NZVI reactivity) with the synthesis variables (X_i) is given by:

$$Y = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} b_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} b_{ij} X_i X_j \quad (3)$$

where b_o, b_i, b_{ii}, b_{ij} are the regression coefficients related to average, linear, quadratic and interaction effects, respectively.

Fitting of the experimental and predicted results was evaluated by ANOVA (Analysis of Variance). The F-test was applied to verify whether the model could predict a significant variation in the experimental data. The statistical analysis was performed using the Statgraphics 16.1.15 software.

2.4. NZVI characterization

The BET surface area (S_{BET}) of the NZVI particles was determined by N_2-physisorption at −196 °C in a TriStar II (Micromeritics) apparatus. The data within the relative pressure (P/P_0) range up to 0.3 were used for S_{BET} calculation. Prior to measurement, the sample was vacuum dried at 150 °C for 12 h, followed by degassing at the same temperature for 4 h in an outgassing station to remove any adsorbed water or entrapped gases. Scanning Electron Microscopy (SEM) images of the highest reactivity NZVI samples were taken in a JEOL, model JEM-4000 EX microscope and X-ray diffraction (XRD) spectra were obtained in a Siemens model D-5000 diffractometer with Cu Kα radiation (λ = 1,54 Å).

2.5. Evaluation of NZVI reactivity

The NZVI samples obtained under the different conditions of the experimental design were tested in the decoloration of DR1 dye in aqueous solution. In each experiment 2.5 mg of nanoparticles was contacted with 50 mL of 0.025 mM DR1 solution and the mixture was stirred at 200 rpm for 10 min and then filtered for analysis. All the runs were carried out by duplicate and standard deviation (SD) was in all cases below 3%. Dye decoloration was calculated as the percentage decrease in absorbance at the wavelength of 502 nm, corresponding to the absorption of the azo chromophore (—N=N—).

2.6. Analytical methods

DR1 degradation was followed by periodically withdrawing and analyzing liquid samples. The catalyst was separated by filtration using a PTFE filter (pore size 0.45 μm). The decoloration of DR1 was measured with a UV–vis spectrophotometer (scanning wavelengths 200–800 nm). The decoloration was calculated as the percentage decrease of absorbance decrease at the maximum wavelength of λ max = 502 nm. The iron dissolved in the reaction medium was measured by the o-phenantroline method using an Agilent Cary 60 UV–vis spectrophotometer. The mineralization was evaluated by measuring the Total Organic Carbon (TOC) with a Shimadzu TOC Analyzer (VSCH). Phenolic compounds were

Table 1
Experimental design.

Variable (symbol)	Levels				
	−α	−1	0	+1	+α
[Fe²⁺], mol/L (X_1)	0.06	0.08	0.1	0.12	0.13
rate, mL/min (X_2)	3.3	5.0	7.5	10	11.7
pH (X_3)	1.3	2.0	3.0	4.0	4.6